distilled off with steam, separated, treated with concentrated sulphuric acid and boiled over metallic sodium with a reflux condenser until all traces of halogen were removed. On distillation the octane boiled at 117.8° at 760 mm. and on analysis gave the following result:

Calculated for	C_8H_{18}:	C, 84.21; H, 15.79
Found:		C, 84.11; H, 15.96

The constitution of 3-methyl-heptane, $CH_3CH_2CH(CH_3)—CH_2CH_2CH_2CH_3$, is shown by the method of preparation.

I am deeply indebted to the C. M. Warren Fund for materials used in this research.

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CONTRIBUTIONS TO OUR KNOWLEDGE OF AMERICAN COLOPHONIUM. I. THE RESIN OF THE NORWAY PINE.

BY GEORGE B. FRANKFORTER.

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The first important work on the resins was begun by Baup[1] in 1826. He obtained from *Pinus abies*, a crystallized substance to which he gave the name abietic acid. From another species, *Pinus maritima*, he obtained a second substance which he called pinic acid. Later, Unverdorben[2] obtained two acids from common colophonium. One seemed to be identical with abietic acid although it was called sylvic acid; the other, an amorphous substance, was called pinic acid, differing in its general properties, however, from Baup's pinic acid. Immediately following the work of Unverdorben, Trommsdorff[3] obtained from American colophonium a crystallized acid which he regarded as sylvic acid and to which he assigned the formula $C_{40}H_{60}O_4$. Some years later Siewert[4] repeated the work of Trommsdorff and assigned to sylvic acid the formula $C_{20}H_{30}O_2$, showing incidentally that abietic acid is isomeric with Baup's pinic and with pimaric acid described by Laurent,[5] differing, however, in its physical properties and especially with regard to its solubility in alcohol.

Maly[6] again studied American colophonium exhaustively, obtaining a crystallized acid by a slightly modified form of the Unverdorben method. Maly's process for the purification of the resin acids has been of the greatest importance, inasmuch as it has been practically the only process used

[1] *Ann. chim. phys.*, **31**, 108.
[2] *Pogg. Ann.*, **11-20**, 239.
[3] *Ann.*, **13**, 169.
[4] *Z. gesammten Naturwissenschaften*, **14**, 311.
[5] *Ann.*, **34**, 372.
[6] *J. prakt. Chem.*, **96**, 145.

by others in the purification of common colophonium. Briefly stated, it is as follows: Crude colophonium is first treated in hot 60 per cent. alcohol. A part of the substance remains undissolved. This is removed and the clear filtrate allowed to stand, when yellowish flakes precipitate out. These flaky crystals are redissolved in hot, 80 per cent. alcohol, and water added until crystals begin to appear. On standing, most of the acid crystallizes out. The process is repeated until the acid is pure. The acid which Maly obtained by this process, however, was not identical with the acid of Unverdorben and Trommsdorff, although it was called abietic acid. The formula given was $C_{44}H_{64}O_5$. Sylvic acid was obtained by the action of sulphuric or hydrochloric acid upon abietic acid.

Later, Flückiger[1] obtained an acid from American colophonium by treating the alcoholic solution with hydrochloric acid gas. This acid was regarded as identical with Maly's abietic acid, its salts and general characteristics, however, differed from those given by Maly. He assigned to it the formula $C_{20}H_{30}O_2$. Kelbe[2] obtained from resin oil an acid which he regarded as abietic acid and to which he gave the formula $C_{44}H_{64}O_5$. Mach[3] in his monograph on abietic acid showed that it is the only acid in the American colophonium, that it differs from pimaric acid, $C_{20}H_{30}O_2$, by having not only different properties, but also a different formula, $C_{19}H_{28}O_2$. Incidentally, it was shown that the second substance found in common colophonium and evidently that regarded as sylvic acid, is only the anhydride of abietic acid. These results were partially corroborated by Loos.[4] Tschirch and Koritschoner[5] again studied the resin from *Pinus palustris* and isolated two acids, one with a formula $C_{13}H_{20}O_2$ palabienic, and the other $C_{20}H_{30}O_2$ palabietic acid. This is significant inasmuch as the substance from which these two acids were obtained was regarded as abietic acid. Henry[6] has shown that the sandarac resins contain pimaric acid but he regarded it as entirely different from abietic acid. Another acid was also isolated to which the formula $C_{30}H_{45}O_5$ was given.

From the work of the last two writers, one may draw the conclusion that each particular resin contains at least one distinct and characteristic acid. In fact, such an assumption as this is the only way by which one may account for the different physical and chemical properties of the different resins.

[1] *J. prakt. Chem.*, **101**, 235.
[2] *Ber.*, **13**, 888.
[3] *Monatsh. Chem.*, **15**, 627.
[4] Diss. Columbia University, 1900.
[5] *Arch. Pharm.*, **240**, 568.
[6] *J. Chem. Soc.*, **79**, 1144.

Abietic acid or one of its isomeric forms seems to be present as a part of most of the resins. The remaining part, however, is usually the acid which gives the resin its characteristic properties. These statements seem to be verified in this paper.

Experimental Part.

The resin used in the following experiments, was obtained from the trees of the Norway pine, *Pinus resinosa*, by the ordinary method of boxing. During the spring months it was not found difficult to obtain sufficient material in this way for experimental work. Immediately after collecting, the pitch was placed in closed vessels and carefully protected from the air and light. It was kept in this condition until the work was begun. The fresh pitch is perfectly colorless and almost as mobile as water. It slowly changes when exposed to the air and sun light, becoming thicker and slightly darker in color. It has a peculiar aromatic odor differing entirely from the southern pitch. It mixes in all proportions with ether, chloroform and absolute alcohol. The specific gravity, $d_4^{20}=0.8137$. The specific rotation $[\alpha]_D^{20} = +4$. Refractive index at 20°, 1.4788. It contains a very small amount of inorganic matter.

Resinic Acid, $C_{25}H_{38}O_5$.—After the preliminary examination of the pitch, the turpentine was removed by gently warming, *in vacuo*, preparatory to the chemical examination of the resin. After the turpentine, which represents about 20 per cent. of the total weight, had been removed, the resin remaining was an almost white solid, and so brittle that it could readily be converted into a powder; melting point, 81–5°. The powder is very soluble in absolute alcohol, ether, chloroform, glacial acetic acid, acetone, benzene, toluene and xylene. It is only slightly soluble in 70 per cent. alcohol and quite insoluble in 60 per cent. alcohol, hence the method of Unverdorben could not be used in the purification of the substance. Treated with caustic soda, the acid dissolved to an almost colorless solution, leaving only a very small amount of insoluble matter. This alkaline solution acidified with hydrochloric acid yielded a waxy instead of a crystalline substance such as Maly obtained from common colophonium. In fact, none of the methods which have been given for the purification of colophonium could be used in the purification of this acid.

The only satisfactory means found for obtaining a well-defined crystalline substance, was by dissolving the powder in the smallest possible quantity of ether or absolute alcohol, decanting off the colorless solution and slowly pouring into 80 per cent. alcohol. If not poured too rapidly and if the alcohol is agitated while the solution is being added, the substance is completely converted into an almost white powder. After reprecipitation several times in this manner the substance had a crystalline appearance. The substance melted at 83–7°. An examination under the microscope showed a distinctly crystalline form but the crystals were not perfect enough to permit accurate measurements.

An average of two analyses gave the following: C, 72.62; H, 9.24. Abietic acid contains C, 79.16; H, 9.73. It is quite evident that this is not abietic acid. The unsatisfactory melting point, however, made further purification necessary.

It was found that the substance could be separated into two apparently distinct substances by dissolving the dried powder in absolute ether, cooling in a freezing mixture and passing perfectly anhydrous ammonia gas into the solution. As soon as the ammonia gas came in contact with the cold ether solution, a beautiful white crystalline powder was precipitated. After passing gas into the solution until there was a distinct odor of ammonia, the cold solution was rapidly filtered and the precipitate washed with dry ether. The insoluble substance after washing was an almost white powder, showing distinct signs of crystallization. It was found to be an unstable

ammonium salt. The freshly made salt was soluble in water and in absolute alcohol but after remaining for some time in the air or even in a vacuum desiccator, a part became insoluble in water but dissolved in ether. An examination showed that both in water and in air the ammonium salt dissociated into free acid and ammonia. The freshly made ammonium salt was dissolved in water and dilute hydrochloric acid added until all of the acid was precipitated. By slowly adding the hydrochloric acid the organic acid came down in a crystalline powder. This was carefully washed with water, dissolved in absolute alcohol and precipitated by pouring into 80 per cent. alcohol. The reprecipitated powder was filtered off and washed with 80 per cent. alcohol. The purified acid still had the same peculiar crystalline-looking appearance. The melting point was now 97–8°. Further purification failed to change this melting point.

Analysis of the dried substance gave the numbers indicated below:

Calculated for $C_{25}H_{36}O_5$:	C, 71.77;	H, 9.09		
	I.	II.	III.	IV.
Found: C,	71.79	71.62	71.83	72.01
H,	9.04	9.13	8.93	8.85

This acid differs from abietic acid, $C_{19}H_{28}O_2$, not only in its composition but also in its physical and chemical properties. The average analysis of abietic acid shows practically 79 per cent. of carbon or 7 per cent. more than the average of the above analysis.

Ammonium Resinate, $C_{25}H_{36}O_5(NH_4)_2$.—That resinic acid has very weak acid properties is indicated by the fact that the ammonium salt begins to decompose immediately after removing from the ammoniacal ether solution, liberating ammonia and the free acid. After standing a year the salt had lost about half of its ammonia. In fact, it gives an alkaline reaction at all times, no doubt due to the liberation of free ammonia. When first prepared, the dissociation is so marked that the odor of ammonia is distinctly noticeable. After one month's exposure to the air the odor of ammonia was not noticeable but there was still an alkaline reaction. The freshly precipitated salt began to melt at 98° and was completely melted at 112°. The unsatisfactory melting point is doubtless due to dissociation as the salt on standing for a long time has a fairly sharp melting point of 114–6°.

Analysis of the freshly precipitated salt which had been washed with dry ether and dried for one hour in a vacuum desiccator gave the following results:

Calculated for $C_{25}H_{36}O_5(NH_4)_2$:	C, 66.37;	H, 9.73;	N, 6.19	
	I.	II.	III.	
Found	C, 66.44	66.44;	N, 5.62	
	H, 9.67	9.33;		

Apparently a part of the ammonia had been lost in drying for one hour. Analysis of the same substance after standing one year gave 3.42 per cent. of nitrogen. This would indicate that the salt after standing one year had changed into the acid salt $C_{25}H_{36}O_5H(NH_4)$.

Calculated for $C_{25}H_{36}O_5H(NH_4)$: N = 3.22. Found: N, 3.42

Barium Resinate, $C_{25}H_{36}O_5Ba$.—To the clear solution of the sodium salt, barium chloride was added in slight excess. The insoluble barium salt was filtered off, and washed with water free from carbon dioxide until the filtrate no longer showed traces of barium. The salt was then dried and analyzed.

Calculated for $C_{25}H_{36}O_5Ba$:	C, 54.25;	H, 6.57;	Ba, 24.77
Found:	C, 53.82;	H, 7.2 ;	Ba, 23.96

The salt is so unstable that even carbon dioxide will decompose it, liberating the free acid.

Abietic Acid, $C_{19}H_{28}O_2$.—The ether solution from the ammonium salt of resinic acid was removed and evaporated. The residue left was a light-colored resinous substance. This soluble part represented about 30 per cent. of the total resin. It was again taken up with ether containing a little dry ammonia gas and filtered. The residue left after allowing the ether to evaporate, was hard and brittle. By repeating this process several times, the substance became almost white. The salt could not be obtained in a distinctly crystalline form. Further purification, however, failed to change the comparatively sharp melting point of 89°.

Calculated for ammonium abietate, $C_{19}H_{27}O_2(NH_4)$: C = 73.77; H = 10.16; N = 4.59
Found: C = 73.44, 73.56, 73.16; H = 9.87, 9.62, 10.22; N = 5.15, 5.93, 4.61.

The amount of nitrogen found above is practically twice as much as was found by Mach who ascribed to the ammonium salt the formula $C_{19}H_{27}O_2(NH_4).C_{19}H_{28}O_2$. This difference is doubtless due to the different methods of preparation. The acid salt, however, could not be prepared either by treating the neutral salt with water or by exposing to the air. In each case, the salt lost more than half of its ammonia. In fact, after long exposure to the air the salt lost nearly all of its ammonia. By triturating the ammonium salt with dilute hydrochloric acid and washing with water in order to remove the ammonium chloride formed together with the excess of the hydrochloric acid, an almost white granular powder was formed. After carefully washing with water, the powder was dissolved in alcohol and water added until precipitation began as indicated by the milky appearance of the solution. It was then set aside until the acid had crystallized out. After crystallizing several times, the acid melted at 129–30°. Analyses gave the following:

Calculated for $C_{19}H_{28}O_2$: C = 79.16 ; H = 9.73
Found: C = 79.02, 78.64; H = 9.64, 10.00

The potassium and barium salts were prepared but as their properties seemed to coincide with those of common abietic acid, no analyses were made.

The Mach formula for abietic acid has been assumed to be the correct one although there is still some doubt. The above analyses, however, agree almost as well with the generally accepted formula $C_{20}H_{30}O_2$.

From the above facts, one may draw the conclusion that the resin of the Norway pine contains two acids. The one is doubtless abietic acid although its melting point is lower than that recently given to abietic acid. The other, resinic acid, differs from any of the resin acids described. It resembles, to some extent, Tschirch's palabienic acid, which was prepared by a somewhat similar method.

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5-BROM-2-AMINOBENZOIC ACID, A NEW PREPARATION.

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The original object of this investigation was to convert trichlorethylidene-*o*-aminobenzoic acid[1] into a compound containing an asymmetric carbon atom by means of bromine or hydrobromic acid, thus

[1] Niementowski and Orzechowski, *Ber*, **28**, 2812; also Wheeler, THIS JOURNAL, **30**, 139.